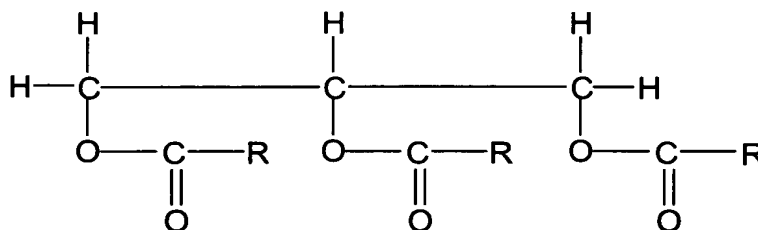


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Demulsifiers For Mixtures Of Middle Distillates  
With Fuel Oils Of Vegetable Or Animal Origin

- [0001] The present invention relates to the use of an additive as a demulsifier for mixtures of middle distillates with vegetable or animal fuel oils and correspondingly additized fuel oils.
- [0002] In view of decreasing world crude oil reserves and the discussion about the environmentally damaging consequences of the use of fossil and mineral fuels, there is increasing interest in alternative energy sources based on renewable raw materials. These include in particular natural oils and fats of vegetable or animal origin. These are generally triglycerides of fatty acids which have from 10 to 24 carbon atoms and a calorific value comparable to conventional fuels, but are at the same time classified as biodegradable and environmentally compatible.
- [0003] Oils obtained from animal or vegetable material are mainly metabolism products which include triglycerides of monocarboxylic acids, for example acids having from 10 to 25 carbon atoms, and correspond to the formula



where R is an aliphatic radical which has from 10 to 25 carbon atoms and may be saturated or unsaturated.

- [0004] In general, such oils contain glycerides from a series of acids whose number and type vary with the source of the oil, and they may additionally contain phosphoglycerides. Such oils can be obtained by processes known from the prior art.
- [0005] As a consequence of the sometimes unsatisfactory physical properties of the triglycerides, the industry has applied itself to converting the naturally occurring triglycerides to fatty acid esters of low alcohols such as methanol or ethanol. The prior art also includes mixtures of middle distillates with oils of vegetable or animal origin (also referred to hereinbelow as „biofuel oils“).
- [0006] EP-B-0 665 873 discloses a fuel oil composition which comprises a biofuel, a fuel oil based on crude oil and an additive which comprises (a) an oil-soluble ethylene copolymer or (b) a comb polymer or (c) a polar nitrogen compound or (d) a compound in which at least one substantially linear alkyl group having from 10 to 30 carbon atoms is bonded to a nonpolymeric organic radical, in order to provide at least one linear chain of atoms which includes the carbon atoms of the alkyl groups and one or more nonterminal oxygen atoms, or (e) one or more of the components (a), (b), (c) and (d).
- [0007] A hindrance to the use of mixtures of middle distillates and biofuel oils is their strong tendency to enter into stable emulsions with water. Such emulsions result in corrosion problems in the distribution chain of the fuel oils, and also when they are used in motor vehicles.
- [0008] It is therefore an object of this invention to find a suitable demulsifier for mixtures of middle distillates and biofuel oils.
- [0009] It has now been found that, surprisingly, ethylene copolymers which contain hydrophilic substituents are excellent demulsifiers for such

mixtures.

- [00010] The present invention provides a fuel oil comprising a major proportion of a mixture of
- A) a middle distillate fuel oil, and
  - B) a biofuel oil,
- and also a minor proportion of
- C) an oil-soluble copolymer of ethylene and at least 0.2 to 35 mol% of a further olefinically unsaturated compound which contains at least one free hydroxyl group, and which has an OH number of from 10 to 300 mg KOH/g.
- [00011] The invention further provides the use of the copolymer defined under C) as a demulsifier in mixtures of middle distillate fuel oils with biofuel oils.
- [00012] The invention further provides a method for demulsifying mixtures of middle distillate fuel oils with biofuel oils by adding the above-defined copolymer to the mixtures.
- [00013] As constituent A), middle distillate fuel oils are used. This refers in particular to those mineral oils which are obtained by distilling crude oil and boil in the range from 120 to 450°C, for example kerosene, jet fuel, diesel and heating oil. Preference is given to using those middle distillates which contain less than 350 ppm of sulfur, particularly preferably less than 200 ppm of sulfur, in particular less than 50 ppm of sulfur and in special cases less than 10 ppm of sulfur. These are generally those middle distillates which have been subjected to refining under hydrogenating conditions, and therefore contain only small fractions of polyaromatic and polar compounds. They are preferably those middle distillates which have 95% distillation points below 370°C, in particular 350°C and in special cases below 330°C. The middle

distillates preferably have aromatic contents of below 28% by weight, in particular below 20% by weight.

- [00014] As constituent B), biofuel oils are used. In a preferred embodiment, the biofuel oil, which is frequently also referred to as „biodiesel“ or „biofuel“ comprises fatty alkyl esters of fatty acids having from 14 to 24 carbon atoms and alcohols having from 1 to 4 carbon atoms. A relatively large proportion of the fatty acids commonly contains one, two or three double bonds. The fatty acids are more preferably, for example, rapeseed oil methyl ester and especially mixtures which comprise rapeseed oil fatty acid methyl ester, sunflower oil fatty acid methyl ester and/or soya oil fatty acid methyl ester.
- [00015] Examples of oils which derive from animal or vegetable material and which can be used in the inventive composition are rapeseed oil, coriander oil, soya oil, cottonseed oil, sunflower oil, castor oil, olive oil, groundnut oil, corn oil, almond oil, palm kernel oil, coconut oil, mustardseed oil, beef tallow, bone oil and fish oils. Further examples include oils which derive from wheat, jute, sesame, shea treenut, arachis oil and linseed oil, and can be derived from these by processes known from the prior art. It is also possible to use oils which have been obtained from used oils such as deep-frying oil. Rapeseed oil, which is a mixture of fatty acids partially esterified with glycerol, is preferred, since it is obtainable in large amounts and is obtainable in a simple manner by extractive pressing of rapeseed. In addition, preference is likewise given to the widely available oils of sunflowers and soya, and also to their mixtures with rapeseed oil.
- [00016] Useful lower alkyl esters of fatty acids include the following, for example as commercial mixtures: the ethyl, propyl, butyl and in particular methyl esters of fatty acids having from 12 to 22 carbon atoms, for example of lauric acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid,

oleic acid, elaidic acid, petroselic acid, ricinoleic acid, elaeostearic acid, linoleic acid, linolenic acid, eicosanoic acid, gadoleic acid, docosanoic acid or erucic acid, which preferably have an iodine number of from 50 to 150, in particular from 90 to 125. Mixtures having particularly advantageous properties are those which contain mainly, i.e. at least 50% by weight of, methyl esters of fatty acids having from 16 to 22 carbon atoms and 1, 2 or 3 double bonds. The preferred lower alkyl esters of fatty acids are the methyl esters of oleic acid, linoleic acid, linolenic acid and erucic acid.

- [00017] Commercial mixtures of the type mentioned are obtained, for example, by hydrolyzing and esterifying animal and vegetable fats and oils by transesterifying them with lower aliphatic alcohols. To prepare lower alkyl esters of fatty acids, it is advantageous to start from fats and oils having a high iodine number, for example sunflower oil, rapeseed oil, coriander oil, castor oil, soya oil, cottonseed oil, groundnut oil or beef tallow. Preference is given to lower alkyl esters of fatty acids based on a new variety of rapeseed oil of whose fatty acid component more than 80% by weight are derived from unsaturated fatty acids having 18 carbon atoms.
- [00018] The mixing ratio of the constituents A and B may vary as desired. It is preferably between A:B = 99.9:0.1 and 0.1:99.9, in particular 99:1 and 1:99, especially 95:5 and 5:95, for example 85:15 and 15:85 or 80:20 and 20:80.
- [00019] Constituent C) is an ethylene copolymer. In a preferred embodiment of the invention, the copolymer has an OH number of from 20 to 250 mg KOH/g, in particular from 25 to 200 mg KOH/g. In a further preferred embodiment, the copolymer has an average molecular weight  $M_w$  of from 700 to 10,000 g/mol.

[00020] The olefinically unsaturated compounds which are present in the copolymer in addition to ethylene are preferably vinyl esters, acrylic esters, mono- and diesters of ethylenically unsaturated carboxylic acids, methacrylic esters, alkyl vinyl ethers and/or alkenes which bear hydroxyalkyl, hydroxyalkenyl, hydroxycycloalkyl or hydroxyaryl radicals. These radicals contain at least one hydroxyl group which may be in any desired position on the radical, but preferably at the chain end ( $\omega$ -position) or in the para-position in the case of ring systems.

[00021] The vinyl esters are preferably those of the formula 1



where  $\text{R}^1$  is  $\text{C}_1$ - $\text{C}_{30}$ -hydroxyalkyl, preferably  $\text{C}_1$ - $\text{C}_{12}$ -hydroxyalkyl, especially  $\text{C}_2$ - $\text{C}_6$ -hydroxyalkyl, and also the corresponding hydroxyalkoxy radicals. Suitable vinyl esters include 2-hydroxyethyl vinyl esters,  $\alpha$ -hydroxypropyl vinyl esters, 3-hydroxypropyl vinyl esters and 4-hydroxybutyl vinyl esters, and also diethylene glycol monovinyl esters.

[00022] The acrylic esters are preferably those of the formula 2



where  $\text{R}^2$  is hydrogen or methyl and  $\text{R}^3$  is  $\text{C}_1$ - $\text{C}_{30}$ -hydroxyalkyl, preferably  $\text{C}_1$ - $\text{C}_{12}$ -hydroxyalkyl, especially  $\text{C}_2$ - $\text{C}_6$ -hydroxyalkyl, and also the corresponding hydroxyalkoxy radicals. Suitable acrylic esters include hydroxyethyl acrylate, hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 3-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate, hydroxyisopropyl acrylate, 4-hydroxybutyl acrylate and glycerol monoacrylate. Equally suitable are

the corresponding esters of methacrylic acid, and also esters of ethylenically unsaturated dicarboxylic acids such as maleic acid, fumaric acid or itaconic acid with diols.

[00023] The alkyl vinyl ethers are preferably compounds of the formula 3



where  $\text{R}^4$  is  $\text{C}_1$ - $\text{C}_{30}$ -hydroxyalkyl, preferably  $\text{C}_1$ - $\text{C}_{12}$ -hydroxyalkyl, especially

$\text{C}_2$ - $\text{C}_6$ -hydroxyalkyl, and also the corresponding hydroxyalkoxy radicals. Suitable alkyl vinyl ethers include 2-hydroxyethyl vinyl ether, hydroxypropyl vinyl ether, hexanediol monovinyl ether, 4-hydroxybutyl vinyl ether, diethylene glycol monovinyl ether and cyclohexanedimethanol monovinyl ether.

[00024] The alkenes are preferably monounsaturated hydroxyhydrocarbons having from 3 to 30 carbon atoms, in particular from 4 to 16 carbon atoms and especially from 5 to 12 carbon atoms. Suitable alkenes include dimethylvinylcarbinol (= 2-methyl-3-buten-2-ol), allyloxypropanediol, 2-butene-1,4-diol, 1-buten-3-ol, 3-buten-1-ol, 2-buten-1-ol, 1-penten-3-ol, 1-penten-4-ol, 2-methyl-3-buten-1-ol, 1-hexen-3-ol, 5-hexen-1-ol and 7-octene-1,2-diol.

[00025] Likewise suitable for use as demulsifiers are copolymers containing structural units which derive from ethylene and vinyl alcohol. Copolymers of this type can be prepared by partially or fully hydrolyzing a copolymer containing structural units which derive from ethylene and vinyl acetate.

[00026] Equally, copolymers which derive from ethylene and monomers which bear glycidyl radicals, for example glycidyl (meth)acrylate or glycidyl

allyl ether, after hydrolysis with water, alcohols such as methanol or glycol, or amines, for example ammonia, methylamine, ethanolamine or diethanolamine can be used in accordance with the invention.

- [00027] Demulsification can also be achieved in the inventive manner by using ethylene copolymers which contain alkoxyated acids groups. Ethylene copolymers suitable for this purpose are, for example, those containing acrylic acid, methacrylic acid, itaconic acid, fumaric acid, maleic acid or maleic anhydride. To this end, these copolymers containing acid groups are alkoxyated on the acid groups with  $C_1$ - to  $C_{10}$ -alkylene oxides. Preferred alkylene oxides are ethylene oxide, propylene oxide and butylene oxide. The alkoxylation is preferably effected using from 0.5 to 10 mol, in particular from 1 to 5 mol and especially from 1 to 2 mol, of alkylene oxide per mole of acid group.
- [00028] The molar proportion of hydroxyl-functionalized comonomers in the copolymer is preferably from 0.5 to 15%, in particular from 1 to 12%.
- [00029] The melt viscosities of the copolymers according to the invention at 140°C are preferably below 10,000 mPas, in particular between 10 and 1000 mPas and especially between 15 and 500 mPas.
- [00030] In addition to ethylene, the copolymers according to the invention contain at least one comonomer having hydroxyl groups. They may also contain further, for example one, two or three, further olefinically unsaturated comonomers. Such olefinically unsaturated comonomers are, for example, vinyl esters, acrylic acid, methacrylic acid, acrylic esters, methacrylic esters, vinyl ethers or olefins. Particularly preferred vinyl esters are vinyl acetate, vinyl propionate and vinyl esters of neocarboxylic acids having 8, 9, 10, 11 or 12 carbon atoms. Particularly preferred acrylic and methacrylic esters are those with alcohols having from 1 to 20 carbon atoms, in particular of methanol, ethanol, propanol,



n-butanol, isobutanol and tert-butanol. Particularly preferred vinyl ethers are hydroxyvinyl ethers. Particularly preferred olefins are those having 3 to 10 carbon atoms, especially propene, isobutylene, diisobutylene, norbornene, 4-methyl-pentene-1 and hexene. Particular preference is given to terpolymers of ethylene, a hydroxy-functionalized comonomer and either vinyl acetate or a vinyl ester of a neocarboxylic acid having from 8 to 12 carbon atoms. When the copolymers contain a further comonomer, its molar fraction is preferably up to 18%, in particular up to 12%.

[00031] The comonomers are copolymerized by known processes (on this subject, cf., for example, Ullmanns Encyclopädie der Technischen Chemie, 4<sup>th</sup> edition, Vol. 19, pages 169 to 178). Suitable are polymerization in solution, in suspension, in the gas phase and high-pressure bulk polymerization. Preference is given to employing high-pressure bulk polymerization which is carried out at pressures of from 50 to 400 MPa, preferably from 100 to 300 MPa, and temperatures of from 50 to 350°C, preferably from 100 to 300°C. The reaction of the comonomers is initiated by radical-forming initiators (radical chain initiators). This substance class includes, for example, oxygen, hydroperoxides, peroxides and azo compounds, such as cumene hydroperoxide, t-butyl hydroperoxide, dilauroyl peroxide, dibenzoyl peroxide, bis(2-ethylhexyl) peroxydicarbonate, t-butyl maleate, t-butyl perbenzoate, dicumyl peroxide, t-butyl cumyl peroxide, di(t-butyl) peroxide, 2,2'-azobis(2-methylpropanonitrile), 2,2'-azobis(2-methylbutyronitrile). The initiators are used individually or as a mixture of two or more substances in amounts of from 0.01 to 20% by weight, preferably from 0.05 to 10% by weight, based on the comonomer mixture.

[00032] The desired melt viscosity of the copolymers for the given composition of the comonomer mixture is adjusted by varying the reaction

parameters of pressure and temperature and optionally by adding moderators. Useful moderators have been found to be hydrogen, saturated or unsaturated hydrocarbons, e.g. propane, aldehydes, e.g. propionaldehyde, n-butyraldehyde or isobutyraldehyde, ketones, e.g. acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, or alcohols, e.g. butanol. Depending on the desired viscosity, the moderators are employed in amounts of up to 20% by weight, preferably from 0.05 to 10% by weight, based on the comonomer mixture.

[00033] The high pressure bulk polymerization is carried out in known high pressure reactors, for example autoclaves or tubular reactors, batchwise or continuously, and tubular reactors have proven particularly useful. Solvents such as aliphatic hydrocarbons or hydrocarbon mixtures, benzene or toluene may be present in the reaction mixture, although the solvent-free procedure has been found to be particularly useful. In a preferred embodiment of the polymerization, the mixture of the comonomers, the initiator and, if used, the moderator, is fed to a tubular reactor via the reactor entrance and also via one or more side branches. The comonomer streams may have different compositions (EP-B-0 271 738).

[00034] The copolymers C) are added to the mixtures comprising A) and B) in amounts of from 0.001 to 5% by weight, preferably from 0.005 to 1% by weight and especially from 0.01 to 0.05% by weight. They can be used as such or else dissolved or dispersed in solvents, for example aliphatic and/or aromatic hydrocarbons or hydrocarbon mixtures, for example toluene, xylene, ethylbenzene, decane, pentadecane, petroleum fractions, kerosene, naphtha, diesel, heating oil, isoparaffins or commercial solvent mixtures such as Solvent Naphtha, ®Shellsol AB, ®Solvesso 150, ®Solvesso 200, ®Exxsol, ®Isopar and ®Shellsol D types. They are preferably dissolved in fuel oil of animal or vegetable origin

based on fatty acid alkyl esters. The additives according to the invention preferably contain 1 - 80%, especially 10 - 70%, in particular 25 - 60%, of solvent.

- [00035] The copolymers C) can be added to the oil to be additized by the methods known from the prior art. When more than one copolymer component is to be used, such components can be introduced into the oil together or separately in any desired combination.
  
- [00036] To prepare additive packages for specific solutions to problems, the copolymers C) can also be used together with one or more oil-soluble coadditives which in themselves improve the properties of crude oils, lubricant oils or fuel oils. Examples of such coadditives are polar compounds which effect paraffin dispersion (paraffin dispersants), alkylphenol-aldehyde resins, polymeric cold flow improvers and also oil-soluble amphiphiles.
  
- [00037] For instance, it has been found that mixtures of the copolymers C) with those copolymers which contain from 10 to 40% by weight of vinyl acetate and from 60 to 90% by weight of ethylene are outstandingly useful. In a further embodiment of the invention, the additives according to the invention are used in a mixture with ethylene/vinyl acetate/vinyl 2-ethylhexanoate terpolymers, ethylene/vinyl acetate/vinyl neononanoate terpolymers and/or ethylene/vinyl acetate/vinyl neodecanoate terpolymers to simultaneously improve the flowability and lubricity of mineral oils or mineral oil distillates. Apart from ethylene, the terpolymers of vinyl 2-ethylhexanoates, vinyl neononanoates or of vinyl neodecanoates contain from 8 to 40% by weight of vinyl acetate and from 1 to 40% by weight of the respective long-chain vinyl ester. Apart from ethylene and from 10 to 40% by weight of vinyl esters and/or from 1 to 40% by weight of long-chain vinyl esters, further preferred copolymers also contain from 0.5 to 20% by weight of olefin having

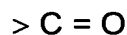
from 3 to 10 carbon atoms, for example isobutylene, diisobutylene, propylene, methylpentene or norbornene.

- [00038] The paraffin dispersants are preferably low molecular weight or polymeric, oil-soluble compounds having ionic or polar groups, for example amine salts, imides and/or amides. Particularly preferred paraffin dispersants contain reaction products of secondary fatty amines having from 8 to 36 carbon atoms, in particular dicoconut fatty amine, ditallow fatty amine and distearylamine. It has been found that paraffin dispersants which are obtained by reacting aliphatic or aromatic amines, preferably long-chain aliphatic amines, with aliphatic or aromatic mono-, di-, tri- or tetracarboxylic acids or their anhydrides are particularly useful (cf. US 4 211 534). Other paraffin dispersants are copolymers of maleic anhydride and  $\alpha,\beta$ -unsaturated compounds, which may optionally be reacted with primary monoalkylamines and/or aliphatic alcohols (cf. EP-A-0 154 177), the reaction products of alkenyl-spiro-bislactones with amines (cf. EP-A-0 413 279 B1) and, according to EP-A-0 606 055 A2, reaction products of terpolymers based on  $\alpha,\beta$ -unsaturated dicarboxylic anhydrides,  $\alpha,\beta$ -unsaturated compounds and polyoxyalkylene ethers of lower unsaturated alcohols.
- [00039] Suitable coadditives which effect paraffin dispersion are, for example, esters. These esters derive from polyols having 3 or more OH groups, in particular from glycerol, trimethylolpropane, pentaerythritol, and also the oligomers which can be obtained therefrom by condensation and have from 2 to 10 monomer units, for example polyglycerol. The polyols have generally been reacted with from 1 to 100 mol of alkylene oxide, preferably from 3 to 70 mol, in particular 5 to 50 mol, of alkylene oxide per mole of polyol. Preferred alkylene oxides are ethylene oxide, propylene oxide and butylene oxide. The alkoxylation is effected by known processes.

- [00040] The fatty acids suitable for the esterification of the alkoxyated polyols preferably have from 8 to 50, in particular from 12 to 30, especially from 16 to 26, carbon atoms. Suitable fatty acids are, for example, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, margaric acid, stearic acid, isostearic acid, arachic acid and behenic acid, oleic acid and erucic acid, palmitoleic acid, myristoleic acid, ricinoleic acid, and also the fatty acid mixtures obtained from natural fats and oils. Preferred fatty acid mixtures contain more than 50% of fatty acids having at least 20 carbon atoms. Preferably, less than 50% of the fatty acids for esterification contain double bonds, in particular less than 10%; they are especially very substantially saturated. In this context, very substantially saturated means an iodine number of the fatty acid used of up to 5 g of I per 100 g of fatty acid. The esterification can also be effected starting from reactive derivatives of fatty acids such as esters with lower alcohols (for example methyl or ethyl esters) or anhydrides.
- [00041] To esterify the alkoxyated polyols it is also possible to use mixtures of the above fatty acids with fat-soluble, polybasic carboxylic acids. Examples of suitable polybasic carboxylic acids are dimer fatty acids, alkenylsuccinic acids and aromatic polycarboxylic acids, and also their derivatives such as anhydrides and C<sub>1</sub>- to C<sub>5</sub>-esters. Preference is given to alkenylsuccinic acids and their derivatives with alkyl radicals having from 8 to 200, in particular from 10 to 50, carbon atoms. Examples are dodecenyl-, octadecenyl- and poly(isobutenyl)succinic anhydride. Preference is given to using the polybasic carboxylic acids in minor proportions of up to 30 mol%, preferably from 1 to 20 mol%, in particular from 2 to 10 mol%.
- [00042] Ester and fatty acid are used for the esterification, based on the content of hydroxyl groups on the one hand and carboxyl groups on the other

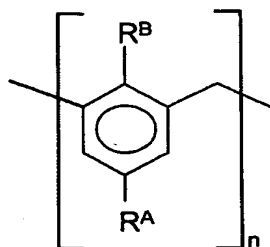
hand, in a ratio of 1.5:1 to 1:1.5, preferably from 1.1:1 to 1:1.1, in particular equimolar. The paraffin-dispersing action is particularly marked when there is an acid excess of up to 20 mol%, especially up to 10 mol%, in particular up to 5 mol%.

- [00043] The esterification is carried out by customary processes. It has been found to be particularly useful to react polyol alkoxyate with fatty acid, optionally in the presence of catalysts, for example para-toluenesulfonic acid, C<sub>2</sub>- to C<sub>50</sub>-alkylbenzenesulfonic acids, methanesulfonic acid or acidic ion exchangers. The water of reaction can be removed distillatively by direct condensation or preferably by means of azeotropic distillation in the presence of organic solvents, in particular aromatic solvents, such as toluene, xylene or else higher-boiling mixtures such as ®Shellsol A, Shellsol B, Shellsol AB or Solvent Naphtha. Preference is given to esterifying to completion, i.e. using from 1.0 to 1.5 mol of fatty acid per mole of hydroxyl groups for the esterification. The acid number of the esters is generally below 15 mg KOH/g, preferably below 10 mg KOH/g, especially below 5 mg KOH/g.
- [00044] Particularly preferred paraffin dispersants are prepared by reacting compounds which contain an acyl group with an amine. This amine is a compound of the formula  $NR^6R^7R^8$  where R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> may be the same or different, and at least one of these groups is C<sub>8</sub>-C<sub>36</sub>-alkyl, C<sub>6</sub>-C<sub>36</sub>-cycloalkyl, C<sub>8</sub>-C<sub>36</sub>-alkenyl, in particular C<sub>12</sub>-C<sub>24</sub>-alkyl, C<sub>12</sub>-C<sub>24</sub>-alkenyl or cyclohexyl, and the remaining groups are either hydrogen, C<sub>1</sub>-C<sub>36</sub>-alkyl, C<sub>2</sub>-C<sub>36</sub>-alkenyl, cyclohexyl, or a group of the formulae  $-(A-O)_x-E$  or  $-(CH_2)_n-NYZ$ , where A is an ethylene or propylene group, x is a number from 1 to 50, E = H, C<sub>1</sub>-C<sub>30</sub>-alkyl, C<sub>5</sub>-C<sub>12</sub>-cycloalkyl or C<sub>6</sub>-C<sub>30</sub>-aryl, and n is 2, 3 or 4, and Y and Z are each independently H, C<sub>1</sub>-C<sub>30</sub>-alkyl or  $-(A-O)_x$ . In this context, an acyl group is a functional group of the following formula:



- [00045] The paraffin dispersants can be admixed with the copolymers C) or added separately to the middle distillate to be additized.
- [00046] Alkylphenol-aldehyde resins are known in principle and described, for example, in Römpp Chemie Lexikon, 9th edition, Thieme Verlag 1988-92, Volume 4, p. 3351ff. The alkyl or alkenyl radicals of the alkylphenol have 6 - 24, preferably 8 – 22, in particular 9 – 18, carbon atoms. They may be linear or preferably branched, and the branch may contain secondary and also tertiary structures. They are preferably n- and isohexyl, n- and isooctyl, n- and isononyl, n- and isodecyl, n- and isododecyl, tetradecyl, hexadecyl, octadecyl, eicosyl and also tripropenyl, tetrapropenyl, pentapropenyl and polyisobutenyl up to C<sub>24</sub>. The alkylphenol-aldehyde resin may also contain up to 20 mol% of phenol units and/or alkylphenols having short alkyl chains, for example butylphenol. For the alkylphenol-aldehyde resin, identical or different alkylphenols may be used.
- [00047] The aldehyde in the alkylphenol-aldehyde resin has from 1 to 10, preferably from 1 to 4, carbon atoms, and may bear further functional groups. It is preferably an aliphatic aldehyde, more preferably formaldehyde.
- [00048] The molecular weight of the alkylphenol-aldehyde resins is preferably 350 – 10 000, in particular 400 - 5000 g/mol. This preferably corresponds to a degree of condensation n of from 3 to 40, in particular from 4 to 20. A prerequisite is that the resins are oil-soluble.

[00049] In a preferred embodiment of the invention, these alkylphenol-formaldehyde resins are those which are oligomers or polymers having a repeating structural unit of the formula



where  $\text{R}^A$  is  $\text{C}_6\text{-C}_{24}$ -alkyl or -alkenyl,  $\text{R}^B$  is OH or  $\text{O-(A-O)}_x\text{-H}$  where A =  $\text{C}_2\text{-C}_4$ -alkylene and  $x = 1$  to 50, and  $n$  is a number from 2 to 50, in particular from 5 to 40.

[00050] The alkylphenol-aldehyde resins are prepared in a known manner by basic catalysis to give condensation products of the resol type, or by acidic catalysis to give condensation products of the novolak type.

[00051] The condensates obtained in both ways are suitable for the compositions according to the invention. Preference is given to the condensation in the presence of acidic catalysts.

[00052] To prepare the alkylphenol-aldehyde resins, an alkylphenol having 6 - 24, preferably 8 - 22, in particular 9 - 18, carbon atoms per alkyl group, or mixtures thereof, are reacted with at least one aldehyde, using about 0.5 - 2 mol, preferably 0.7 - 1.3 mol and in particular equimolar amounts of aldehyde, per mole of alkylphenol compound.

[00053] Suitable alkylphenols are in particular n- and isohexylphenol, n- and isooctylphenol, n- and isononylphenol, n- and isodecylphenol, n- and isododecylphenol, tetradecylphenol, hexadecylphenol, octadecylphenol,



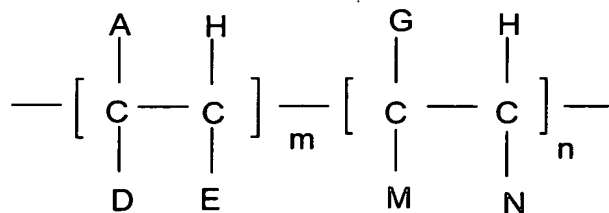
eicosylphenol, tripropenylphenol, tetrapropenylphenol and poly(isobutenyl)phenol up to C<sub>24</sub>.

- [00054] The alkylphenols are preferably para-substituted. The alkylphenols may bear one or more alkyl radicals. The proportion substituted by more than one alkyl group is preferably at most 5 mol%, in particular at most 20 mol% and especially at most 40 mol%. At most 40 mol%, in particular at most 20 mol%, of the alkylphenols used preferably bear an alkyl radical in the ortho-position. Especially, the alkylphenols are unsubstituted by tertiary alkyl groups in the ortho-position to the hydroxyl group.
- [00055] The aldehyde may be a mono- or dialdehyde and bear further functional groups such as –COOH. Particularly suitable aldehydes are formaldehyde, acetaldehyde, butyraldehyde, glutaraldehyde and glyoxalic acid, preferably formaldehyde. The formaldehyde may be used in the form of paraformaldehyde or in the form of a preferably 20 – 40% by weight aqueous formalin solution. It is also possible to use corresponding amounts of trioxane.
- [00056] Alkylphenol is customarily reacted with aldehyde in the presence of alkaline catalysts, for example alkali metal hydroxides or alkylamines, or of acidic catalysts, for example inorganic or organic acids, such as hydrochloric acid, sulfuric acid, phosphoric acid, sulfonic acid, sulfamido acids or haloacetic acids, and effected in the presence of an organic solvent which forms an azeotrope with water, for example toluene, xylene, higher aromatics or mixtures thereof. The reaction mixture is heated to a temperature of from 90 to 200°C, preferably 100 - 160°C, and the water of reaction formed is removed during the reaction by azeotropic distillation. Solvents which release no protons under the conditions of the condensation can remain in the products after the condensation reaction. The resins may be used directly or after

neutralization of the catalyst, optionally after further dilution of the solution with aliphatic and/or aromatic hydrocarbons or hydrocarbon mixtures, for example petroleum fractions, kerosene, decane, pentadecane, toluene, xylene, ethylbenzene or solvents such as ®Solvent Naphtha, ®Shellsol AB, ®Solvesso 150, ®Solvesso 200, ®Exxsol, ®ISOPAR and ®Shellsol D types.

[00057] Finally, in a further embodiment of the invention, the additives according to the invention are used together with comb polymers. This refers to polymers in which hydrocarbon radicals having at least 8, in particular at least 10, carbon atoms are bonded to a polymer backbone. These are preferably homopolymers whose alkyl side chains have at least 8 and in particular at least 10 carbon atoms. In copolymers, at least 20%, preferably at least 30%, of the monomers have side chains (cf. Comb-like Polymers-Structure and Properties; N.A. Platé and V.P. Shibaev, J. Polym. Sci. Macromolecular Revs. 1974, 8, 117 ff). Examples of suitable comb polymers are, for example, fumarate/vinyl acetate copolymers (cf. EP 0 153 76 A1), copolymers of a C<sub>6</sub>-C<sub>24</sub>-α-olefin and an N-C<sub>6</sub>-C<sub>22</sub>-alkylmaleimide (cf. EP-A-0 320 766), and also esterified olefin/maleic anhydride copolymers, polymers and copolymers of α-olefins and esterified copolymers of styrene and maleic anhydride.

[00058] Comb polymers can be described, for example, by the formula



In this formula:

A is R', COOR', OCOR', R''-COOR' or OR';

- D is H, CH<sub>3</sub>, A or R;  
 E is H or A;  
 G is H, R", R"-COOR', an aryl radical or a heterocyclic radical;  
 M is H, COOR", OCOR", OR" or COOH;  
 N is H, R", COOR", OCOR, COOH or an aryl radical;  
 R' is a hydrocarbon chain having 8-150 carbon atoms;  
 R" is a hydrocarbon chain having from 1 to 10 carbon atoms;  
 m is a number between 0.4 and 1.0; and  
 n is a number between 0 and 0.6.

[00059] The mixing ratio (in parts by weight) of the copolymers C) with polymeric cold flow improvers, paraffin dispersants, comb polymers and resins is in each case from 1:10 to 20:1, preferably from 1:1 to 10:1.

[00060] The copolymers C) can be used alone or else together with other additives, for example with other solidification point depressants or dewaxing auxiliaries, with corrosion inhibitors, antioxidants, lubricity additives, sludge inhibitors, dehazers and additives for lowering the cloud point.

#### Examples

[00061] Characterization of the test oils:  
 The CFPP value is determined in accordance with EN 116, the boiling characteristics in accordance with ASTM D-86 and the cloud point in accordance with ISO 3015.

**Table 1: Analysis of the biodiesel used (also referred to hereinbelow as "RME" )**

Chain lengths	Fraction
First runnings	0.12
C12	0.01
C13 + iso C14	0.01
C14: 0	0.05
C14:1	0.0
C15 + iso-C16	0.05
C16: 0	4.64
C16: 1/2/3	0.28
C17 + iso-C18	0.11
C18: 0	0.37
C18: 1 trans + cis	61.72
C18: 2 trans + cis	19.16
C18: 3	9.01
C19 + iso-C20	0.29
C20: 0	0.70
C20:1/2/3	1.57
C21 + iso C22	0.26
C22: 0	0.36
C22: 1/2/3	0.39
C24 0	0.15
C23 + iso C24	0.16
C24: 1/2/3	0.18
Final runnings	0.41
	100.00

Iodine number calculated from GC

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Table 2: Characterization of the middle distillates used

	F1	F2	F3	F4
Sulfur content, ppm	7.9	4.9	32.0	900
Density, g/cm <sup>3</sup>	0.8436	0.8306	0.8348	0.8487
Initial boiling point, °C	209.9	143.9	209.1	203.7
Final boiling point, °C	334.6	363.2	347.8	365.6
Boiling range (90-20), °C	63.5	87.6	83.8	94.9
Aromatics content, % by wt.	25.7	16.5	20.5	29.9

[00062] Characterization of the copolymers

[00063] The following copolymers were used:

- P1 E/VA/4-hydroxybutyl vinyl ether (4-HBVE) terpolymer
- P2 E/VeoVa-10/hydroxypropyl acrylate (HPA) terpolymer
- P3 E/VA/hydroxybutyl vinyl ether (HBVE) terpolymer
- P4 E/VA/hydroxybutyl vinyl ether (HBVE) terpolymer
- P5 E/VA/Hydroxyethylvinylether (HEVE)- Terpolymer
- P6 E/VA/hydroxypropyl methacrylate terpolymer
- P7 E/VA/2-methyl-3-buten-2-ol terpolymer
- P8 E/VA copolymer
- P9 E/VA/VeoVa10 terpolymer
- P10 E/VA/VeoVa10 terpolymer

VA = vinyl acetate

VeoVa 10 = vinyl neodecanoate

[00064] For the purposes of the present invention, the OH numbers are determined in accordance with DIN 53240 by reacting with a defined amount of excess acetic anhydride and subsequently titrating the acetic acid formed.

Table 3: Characterization of the copolymers

Polymer	Vinyl acetate	Contents in % by wt.		V <sub>140</sub> , mPa.s	OH number
		VeoV a 10	Of Hydroxy comonomer		
P1	29.1	-	4.2	53	20
P2	-	23.6	34.8	135	121
P3	22.2	-	13.7	88	66
P4	24.1	-	7.3	99	35
P5	21	-	11.5	96	71
P6	11.3	-	36.6	169	112
P7	26.4	-	0.77	131	5
P8	32	-	-	125	0
P9	31	8	-	110	0
P10	31.5	4.1	-	170	0

[00065] Effectiveness as a demulsifier

[00066] The emulsification tendency of additives is tested in accordance with ASTM

[00067] D 1094-85. 80 ml of a diesel fuel are admixed in a 100 ml measuring cylinder with 250 ppm of the additive to be tested and heated to 60°C for 15 minutes and then agitated. After cooling to room temperature, 20 ml of buffer solution are added and the cylinder is agitated for 2 minutes. After 5 minutes, the sample is assessed visually by the following criteria:

Assessment of the separation layer		Assessment of the phase separation	
1	Clear and clean	1	Complete absence of all emulsions and/or deposits in both phases or on the top of the oil phase.
1b	small, clear bubbles which are estimated not to cover more than 50% of the separating layer. No streaks, no film formation or other wetting on the separating layer.	2	As (1), but additionally small air bubbles or small water droplets in the oil phase.
2	Streaks, film formation or other wetting on the separating layer	3	Emulsions and/or deposits in both phases or on the top of the oil phase, and/or drops in the water phase or adhering to the wall (excluding the wall above the oil phase). In brackets: amount of the water phase
3	Narrow border or slight foam formation, or both		
4	Thick border or extensive foam formation, or both		

**Table 4: Effectiveness of copolymers as a demulsifier in a mixture of 95% by weight of F2 and 5% by weight of biodiesel**

Ex. No.	Copolymer	visual assessment					Active ingredient dosage ppm
		Separation layer	Phase separation		Oil phase	Water phase	
1 (C)	none	3-4	14 ml	3	cloudy	clear	-
2 (C)	P8	3	18 ml	3	cloudy	clear	250
3 (C)	P9	4	16 ml	3	cloudy	clear	250
4 (C)	P10	3	18 ml	3	cloudy	clear	250
5	P1	1b*	20 ml	3	cloudy	clear	250
6	P2	1*	20 ml	3	cloudy	clear	250
7	P3	1*	20 ml	3	cloudy	clear	250
8	P6	1*	20 ml	3	cloudy	clear	250
9	P7	1*	20 ml	3	cloudy	clear	250
10	P3	1*	20 ml	3	cloudy	clear	250
11	P3	1*	20 ml	3	cloudy	clear	100
12	P3	1*	20 ml	3	cloudy	clear	50
13	P3	1*	20 ml	3	cloudy	clear	25
14	P3	1*	20 ml	3	cloudy	clear	10
15	P6	1*	20 ml	3	cloudy	clear	250
16	P6	1b*	20 ml	3	cloudy	clear	100
17	P6	1b*	20 ml	3	cloudy	clear	50
18	P6	1b	20 ml	3	cloudy	clear	25
19	P6	2	20 ml	3	cloudy	clear	10
20	P2	1*	20 ml	3	cloudy	clear	250
21	P2	1b*	20 ml	3	cloudy	clear	50
22	P7	1b*	20 ml	3	cloudy	clear	250
23	P7	1b*	20 ml	3	cloudy	clear	50

\* distinct phase separation even after only a short time (1 to 2 min.)



Table 5: Influence of different mixing ratios between middle distillate and biofuel on the emulsification performance

Example	Middle distillate	Biofuel	Copolymer	visual assessment				Active ingredient dosage ppm
				Separation layer	Phase separation	Amount of water phase	Oil phase	Water phase
24 (C)	90 % F1	10 %	-	3-4	3	8 ml	cloudy	clear
25 (C)	95 % F1	5 %	-	1b	3	20 ml	cloudy	clear
26	90 % F1	10 %	P3	1	3	20 ml	cloudy	clear
27 (C)	90 % F2	10 %	-	3-4	3	8 ml	cloudy	clear
28 (C)	95 % F2	5 %	-	3-4	3	14 ml	cloudy	clear
29	90 % F2	10 %	P3	1-2 relatively large clear air bubbles	3	20 ml	cloudy	clear
30 (C)	90 % F3	10 %	-	4	3	15 ml	cloudy	clear
31 (C)	95 % F3	5 %	-	4	3	10 ml	cloudy	clear
32	90 % F3	10 %	P3	1-2 relatively large clear air bubbles	3	20 ml	cloudy	clear

- [00068] Influence of the copolymer containing hydroxyl groups on the action of cold flow improvers
- [00069] A middle distillate having a CFPP of  $-7^{\circ}\text{C}$  and its mixture with 5% of the biofuel described (CFPP of the mixture likewise  $-7^{\circ}\text{C}$ ) with cold flow improver and copolymer containing hydroxyl groups were investigated.

Table 6: Influence on the cold flow properties by copolymers containing hydroxyl groups

Example	Fuel oil	Copolymers			
		300 ppm P8	300 ppm P9	300 ppm P8 + 10 ppm P4	300 ppm P9 + 10 ppm P4
33 (C)	Middle distillate	- 16	- 15	- 17	- 17
34	Middle distillate + biofuel	- 17	- 16	- 17	- 16

- [00070] Influence of the copolymers containing hydroxyl groups on the emulsification performance of the diesel/biodiesel mixture in the presence of flow improvers
- [00071] The emulsification performance of the oil F4 with the addition of 5% by weight of biofuel was distinctly altered by adding 10 ppm of P4 and exhibited hardly any emulsification tendency despite the presence of 300 ppm of a flow improver.

**Table 7: Influence of cold flow improvers on the emulsification tendency with and without copolymer C)**

Ex.	Oil	visual assessment					Active ingredient dosage ppm
		Separation layer	Phase separation		Oil phase	Water phase	
35 (C)	F4	1b	20 ml	3	cloudy	clear	-
36 (C)	F4+RME	3	18 ml	3	cloudy	clear	-
37	F4+RME	1*	20 ml	3	cloudy	clear	10
38 (C)	F4+RME	3	18 ml	3	cloudy	clear	250
39	F4+RME	1b	20 ml	3	cloudy	clear	10
40 (C)	F4+RME	3	18 ml	3	cloudy	clear	250
41	F4+RME	1b	20 ml	3	cloudy	clear	10